STUDIES ON PLASMA PROCESSING OF BLUE DUST

THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF
MASTER OF TECHNOLOGY

In

Metallurgical & Materials Engineering

By

SUMANT KUMAR SAMAL

DEPARTMENT OF METALLURGICAL & MATERIALS ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY,
ROURKELA, INDIA

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Under the Guidance of
Prof. S C Mishra

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Declaration

I hereby declare that, the work which is being presented in this thesis entitled “Studies On Plasma Processing Of Blue Dust” in partial fulfilment of the requirements for the award of M.Tech degree, submitted to the Department of Metallurgical & Materials Engineering, National Institute of Technology, Rourkela, is an authentic record of my own work under the supervision of Prof. S.C. Mishra. I have not submitted the matter embodied in this thesis for the award of any other degree or diploma to any other university or Institute.

Date:26-May-14 **Sumant Kumar Samal**

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CERTIFICATE

This is to certify that, the thesis entitled "Studies on Plasma Processing Of Blue Dust" being submitted to the National Institute of Technology, Rourkela by Mr. Sumant Kumar Samal, Roll no. 212MM1452 for the award of M.Tech degree in Metallurgical & Materials Engineering, is a bonafide record of research work carried out by him under my supervision and guidance.

The candidate has fulfilled all the prescribed requirements. The Thesis which is based on candidate's own work has not been submitted elsewhere for award of any degree.

In my opinion, the thesis is of standard required for the award of M.Tech degree in Metallurgical & Materials Engineering.

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I am especially grateful to DISIR Laboratory supporting staffs without them the work would have not progressed.

Sumant Kumar Samal

CONTENTS

Abstract

A huge amount of blue dust is produced during mining operations of iron ore and mostly dumped at mines site. Till date no measure action is being taken for utilization of blue dust for extraction of metallic iron. Generally metallic iron is produced through BFO and DRI processes where particle/ore size and reductant is the most important factor considered for BF charge. The present piece of research work is aimed at use of blue dust for production of metallic iron. A newly emerging technology i.e. plasma smelting process is adopted for reduction of blue dust. Blue dust of average particle size about 100-150 micron is taken and carbon (pet coke) of 5, 10, 12, 15 and 20 percent is thoroughly mixed, used as feed material. It is charged to a 35 KW dc arc plasma furnace and smelted for different time lengths i.e. 10, 17 and 20min using argon and nitrogen, separately, as plasma forming gas. The degree of metallization, amount of recovery for all samples is measured. Maximum of 86% recovery and 98% metallization is achieved. It is observed that use of nitrogen as plasma forming gas increases the rate of recovery than that of argon plasma, due to high energy flux of nitrogen gas which increases the enthalpy due to its di-atomicity. The X-ray diffraction analysis shows the presence of ferrite and cementite phases in the smelted product. Variation of microstructure is observed with the samples. The hardness measurement of different phases on the sample ensured the presence of ferrite, pearlite and cementite phases depending on smelting condition.

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Chapter 1

INTRODUCTION

- Research Background
- Objectives of Research

Chapter 1
Introduction

1.1 RESEARCH BACKGROUND

In the present era, embryonic technologies comprehends some of the most conspicuous on-going progresses, improvements, and research to expand extraction of iron by using different types of modern technology to achieve an economic process that suits best. Critical components and complex operating conditions are the key factors for reduced utility of input feed material and energy. The need for higher efficiency and productivity across the entire spectrum of iron and steel making industries has ensured that most economic, least time consuming and simplified process is yet to be optimized.

Currently iron and steel making is dominated by the route comprising a blast furnace and a basic oxygen converter; meanwhile Ferro alloys are formed in submerged-arc electric smelting furnaces. The elevated temperatures and thermodynamic energy required by the process can be obtained in two ways; by combustion, or by the use of electrical power. Production on reliable source of high quality raw materials such as sinter, pellets, and coke are the principal economic constraints of the process. In addition the inflexibility of the process capacity, high capital and operation costs, and energy lost in between stages still a prominent aspect for reduced economy. Extraction of pig iron through this route persists some major cons cited below, which can be considered with importance;

- Energy losses in iron oxide feed preparation
- Critical cost machineries : iron oxide feed, energy, and capital costs
- Residence time in the reactor
- Inflexibility of process: cannot be shut down and resumed easily.

Apart from all these there persists another foremost problem in size of iron ore to be processed. Extensive mechanized mining and advanced beneficiation methods to meet the oxide feed requirements of Blast furnace, Direct Reduction and Smelting Reduction processes are resulting in generation of macro and micro fines not only in various mine sites but also crushing units, washing units, and many more. However a part of the fines, mostly macro ones, in the agglomerated form, that is either as .sinter or pellet have found use in various iron making processes, the difficulty still persist with utilization of micro fines.

Blue dust is a high grade soft hematite ore fines containing more than 96 % Fe_2O_3 enormously available today. For transportation problem and environmental hazardous factor concerned, these high grade iron ore fines are getting dumped at mine sites. Utilization of these iron oxide fines and applicability of the same for the blast furnace feed and powder metallurgy is an approach for production of value added product being wasted.

Keeping above facts in sight, application of plasma technology seems to be an emerging alternative for iron and steel making industries for many of its advantages over any other processes. Maximum utilization of heat energy at extreme temperatures is only feasible by plasma that leads to faster rate of reaction with economy. For its wide range of melting material, independency of size and composition of feed, flexibility of controlled operating parameters and purity level in final product has been drawing attention of researchers in the present era.

In general plasma is used as heat source instead of reductant itself as % of degree of reduction lags behind when utilized as reductant.

The selection of type of plasma and preferred operating parameters along with type of reductant is a crucial factor which needs to be considered sensibly in relation to the treating of material. The wrong choice can affect both, trouble shooting and also processing costs. Criteria for selection must be based on answering many questions, which comprises;

i. Type of reducing agent (carboneous or any other)
ii. Type of plasma forming gas (inert, self-reducing self-burning or helps in burning)
iii. Type of process (melting, smelting or smelting reduction)
iv. Process duration
v. Process environment (open air, inert or vacuum)
vi. Feed rate
vii. Power control

1.2 OBJECTIVES OF RESEARCH

The objective of the current study is as follows:

- To explore the extraction of iron from blue dust by varying % of reductant added, types of plasma forming gas used and smelting duration.
- To determine extent of degree of metallization and recovery by altering above parameters.
- X-ray diffraction studies to find out the presence of formation of different phases.
- Optical micrographic studies.
- Measurement of hardness.

Chapter 2

Literature Survey

- Introductory statement
- Plasma
- Types of plasma
- Plasma chemistry
- Generation of plasma
- Application of plasma
- Advantages of plasma over conventional processes
- Iron making Processes
- Reduction kinetics
- Application of plasma technology in smelting and reduction

Chapter 2
Literature Survey

2.1 INTRODUCTORY STATEMENT

This chapter refers to the literature survey of the area of plasma processing of blue dust. This describes the most interesting topic plasma technology and its applicability on extractive metallurgy. It gives a sound description of generation of plasma and its different characteristics. The plasma chemistry under various conditions has been reviewed along with the corresponding research when implemented to a variety of minerals and materials. Blue dust is still a challenge for conventional iron making industries through blast furnace for its fineness. Some of special features of plasma technology like achieving high temperature with liberation of huge heat energy, faster rate of reaction and accessibility to range of materials are of interest of this work.

2.2 Plasma

It is not unusual to refer plasma as the fourth state of matter as it is an ionized gas comprised of molecules, atoms, ions (in their ground or in various excited states), electrons and photons [1,2,4]. Plasma possesses a unique property known as quasi-neutrality, since plasma is electrically neutral.

In contrast to an ordinary gas, plasma encloses free electric charges that are commonly produced from the gas itself by a variety of ionization processes. In a steady-state situation, the rate of ionization in the plasma is balanced by the rate of recombination. Depending upon the energy content of the plasma, the degree of ionization may be so high that virtually no neutral particles are left, i.e. plasma becomes fully ionized.

2.3 Types of plasma

Since plasma is a broad topic as concerned, all together plasmas are classified into three main categories [1, 4]:

- CTE plasmas (Complete thermodynamic equilibrium)
- LTE plasmas (local thermodynamic equilibrium)
- Non-LTE plasmas (nonlocal thermodynamic equilibrium)

Among above three types CTE plasmas are used for thermonuclear fusion experiments. The latter two types are used as laboratory plasmas and also implemented for industrial purposes like MINTEK, South Africa.

Again according to density and energy, typical plasmas are categorized as shown in Fig2.1;

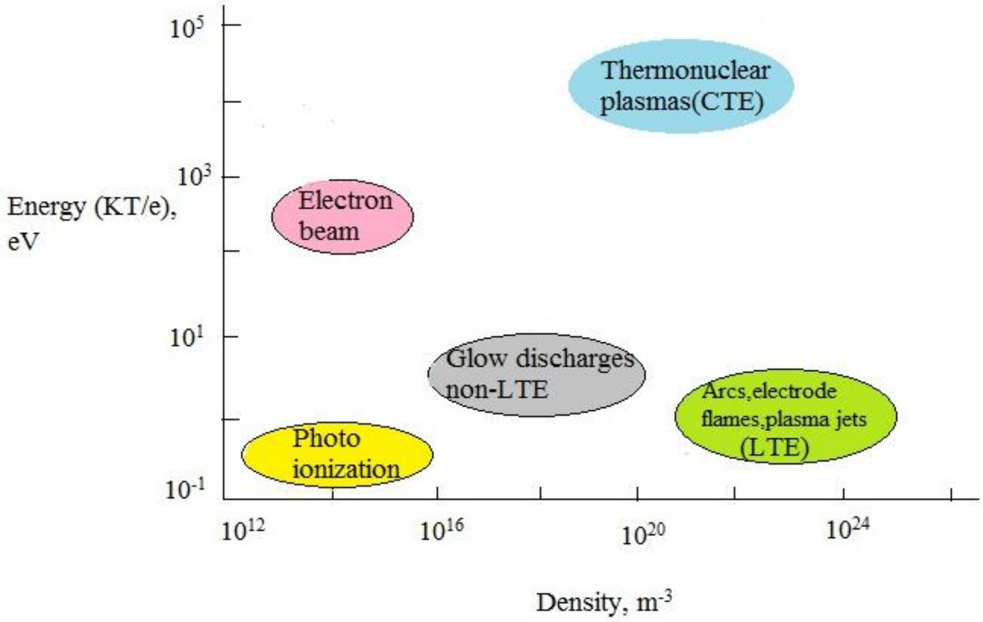


Fig 2.1 Typical plasmas characterized by their energies and densities.

Plasmas generated by electron and photon belong to nonlocal thermodynamic equilibrium category. LTE plasmas are also called as hot plasmas or thermal plasmas or and non-LTE plasmas as cold plasmas or non-thermal plasmas. Basing on temperature plasmas are sub categorized into two groups i.e. low temperature plasma and high temperature plasma. Reactions in plasmas with temperatures below 10^5 ^{0}K or in other words energies less than 10 eV per particle is to be called as low temperature plasmas. Beyond this limit it is said to be high temperature plasma. It is also not unusual plasma to be called as per its gas name i.e. oxygen plasma, argon plasma, nitrogen plasma or argon-nitrogen plasma etc.

2.4 Plasma chemistry

Plasma chemistry refers to the thermodynamic characteristics of several plasma forming gases. Both monoatomic and diatomic gases like argon, helium, neon, nitrogen, oxygen, hydrogen, carbon monoxide, carbon dioxide, air and mixture of gases are used as plasma forming gases.

The relation between energy and temperature of some commonly used monoatomic and diatomic gases are shown in **Fig 2.2.**

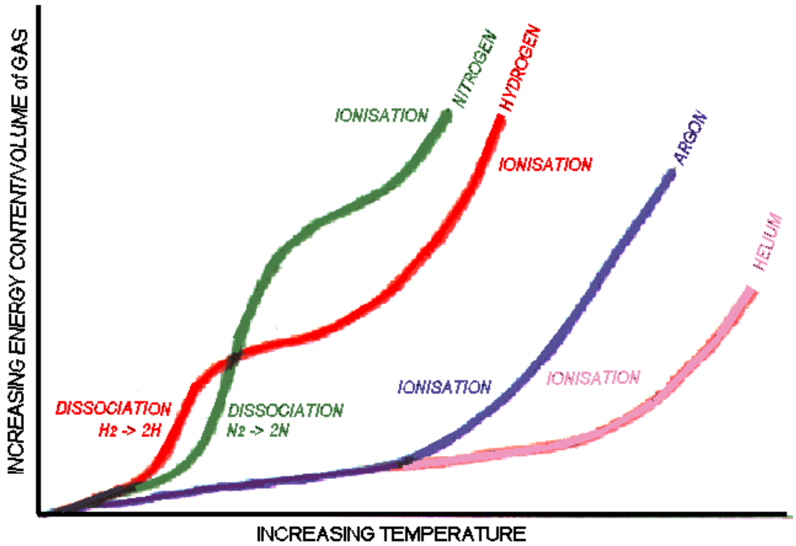


Fig 2.2 Temperature and energy relationship of various plasma gases.

The diatomic molecules require 90 to 200 kcal mole^{-1} to dissociate between 4000 to 10,000^{0}K, while ionization requires 340 to 600 kcal mole^{-1} between 10,000 to 30,000^{0}K [4]. The upper practical limit of flame temperature is about 3500^{0}K, where molecules begin to dissociate, while lower limit of plasma temperatures is about 10,000^{0}K. As most laboratory plasmas are heated electrically, their temperatures will lie in bottom end of ionization curve i.e. above 10000^{0}K for diatomic gases.

For any process operating below 1000^{0}K an air-fuel flame (~2000^{0}K) or an oxygen-fuel flame (~3000^{0}K) will have a high percentage of energy available for the process. However for reaction occurring at 2500^{0}K, only one sixth of energy contained in an oxygen flame will be available and rest must be either wasted or recovered in expensive heat exchangers. On the other hand, a plasma flame composed of atomic nitrogen at 10,000^{0}K would have more than 90% of its energy available above 2500^{0}K. This high energy efficiency may more than offset of the economic advantage that combustion energy over electrical energy; certainly this advantage will increase as electrical energy cheaper while fossil energy gets more expensive.

Although by utilizing plasma high temperature can be achieved with liberation of huge heat energy in a chemical reaction, it is generally not used as reactant in the reaction itself.

2.5 Generation of Plasma

Thermal arc plasmas are generated by striking an electric arc between two or more electrodes. They are characterized by high current densities (greater than 100 A/cm^2) and are more luminous than other types of discharges, especial1y when operated, at atmospheric pressure and above. Thermal arcs can be initiated in several ways. Two common methods are electrode contact which produces a short circuit, or pre-ionization of the gap between electrodes by a high frequency spark. The cathode must be heated beyond 3500 K, at which point thermionic emission of e1ectrons begins, generating the charge carriers that create the plasma state [2]. Cold cathodes are cylindrical and made of heavily cooled copper, Iron, or copper alloy whi1e high temperature cathodes are usually rod-shaped and made of thorium, tungsten or graphite.

Thermal arc plasma torches can operate in two modes i.e. non-transferred and transferred arc. If the plasma torch having two electrodes designed in such a way that hot gas emerges through one electrode and then heated by the flame is called as non-transferred. If there is only one electrode in torch and material to be heated/melted acts as another electrode, then it is said to be transferred. Schematic of both transferred and non-transferred arc plasma torches are shown in the **Fig 2.3**

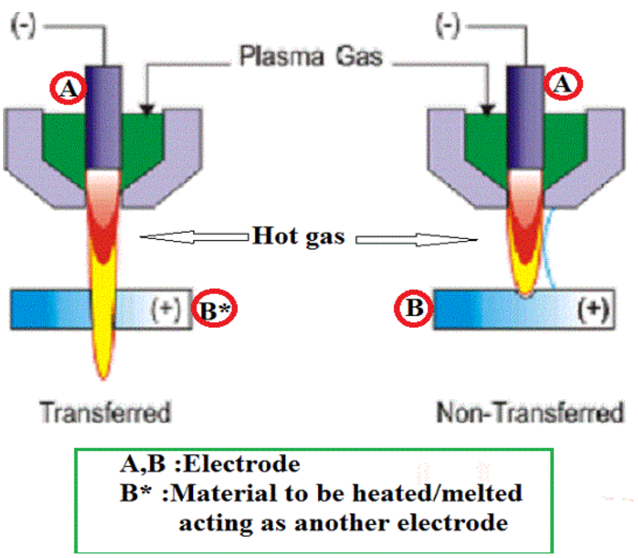


Fig 2.3 Schematic diagram of transferred and non-transferred plasma torches.

2.6 Application of plasma

In last two decades for researchers plasma has claimed to be an emerging solution to a numerous processes due its some unique features and hence implemented in various sectors. Plasma finds significant industrial applications as following processes [3];

- Melting
- Smelting
- Smelting and reduction
- Remelting and refining
- Spark plasma sintering
- Surface modification
- Surface coating

Past research works describes the feasibility of plasma in above cited processes were successful [2, 3, 5, 7]. For reaching high temperature in a reaction, plasma is being preferred and its flexibility over operating parameters along with acceptance of all most all materials and size and shape of material has raised the importance of utilizing plasma [1].

2.7 Advantages of plasma technology over conventional processes

Although there are lot many advantageous aspects behind the utilization of plasma, some of the important features are outlined below.

- **High efficiency**

Since huge amount of energy in the form of heat is available by utilization of plasma, high throughput can be achieved.

- **Long range of melting materials**

Since high temperature can be achieved in a reaction by using plasma, all most all materials can be melted in this process. Although its commercial use to melt and process metals is well known, the method is less well known as a method of melting glass [6].

- **Feed capability**

This process is independent of size, shape and composition of feed material. This ability draws attention of researchers and industries for utilization of high grade fine particles that was a challenge to be processed and dumped due to environmental hazards [15].

- **Transient process**

Due to release of huge heat energy that a particular reaction requires at a particular temperature, plasma stands ahead of any other process to respond the changes in shorter period [6].

- **High energy fluxes**

Higher temperatures with extreme jet velocities and greater thermal conductivities of plasma gases are the key factors that results in high energy fluxes. Smaller furnace dimensions with high smelting capacity are an exceptional aspect of using plasma. [1]

- **Independent energy source**

Flexibility of control over feed rate and power independently and input power is not limited by electrical conductivity of feed material to be melted or smelted. Hence greater freedom of choice with respect to charge composition is available by using plasma.

- **Gas flow rate control**

Unlike combustion systems the gas flow rate, temperature and energy input are not interdependent and gas flow rate and temperature can be controlled separately irrespective of energy input.

- **Gas environment control**

Energy can be provided to system with desired oxygen potential in order to ensure oxidizing, reducing or inert gas conditions independently without taking temperature into account.

- **Electrical energy intensive**

Minimization of the usage of fossil fuel energy and conserve fossil fuel can be made.

- **Purity level of output**

Purity level of final product through plasma processing is very high [23].

- **Economic process**

As output heat energy dominates input combustion energy plasma processing ascertains to be an economic as compared to any other conventional processes. [1]

2.8 Iron making processes

Importance of traditional iron making through blast furnace has been declined due to lots of problems associated, initial investment cost, availability of huge raw feed and complexity in stages. Now a day's production of iron is made in two different forms [5]:

a) Direct reduced iron(DRI)

b) Hot metal(via smelting reduction)

2.8.1Direct reduced iron

In this process iron ore (fines, lumps or pellets) is reduced to the solid-state either by solid or gaseous reducing agents giving rises to a solid final product.

Shaft furnaces, fluidised beds or retorts are used as reactors in case of gas based direct reduction processes. In other hand rotary kilns, rotary hearth furnaces or multi-hearth furnaces are implemented in case of direct reduction processes.

Pros and cons of DRI over BF iron making

Some of advantageous features of DRI are listed below.

i. Independency on coking coal
ii. Smaller module size
iii. Lower initial capital investment
iv. Lesser complexity

Simultaneously there are some draw backs of DRI as well.

i. Final product being solid requires melting for steel making
ii. Smaller module size also affects economy
iii. Productivity lower

Uses of DRI

Direct reduced iron finds its utilization in following places.

- BOF(Basic oxygen furnaces)
- EAF(Electric arc furnaces)
- Induction furnaces
- Open hearth furnaces
- Ladle furnaces

2.8.2 Smelting and reduction (hot metal)

Smelting and reduction involves both reduction and smelting. Basically SR is a two-step operation to obtain liquid hot metal. Lump ores, ore fines, wastes all can be taken as oxide feed in case of smelting reduction. SR may be classified into two categories according to the number of stages involved i.e. single-stage and two stage process. In single stage both reduction and melting occurs in a single reactor where as in case of two-stage two reactors involved for pre-reduction and smelting reduction operations. Further SR processes are classified in terms of smelting furnace used i.e. basic oxygen furnace (BOF), blast furnace hearth (BFH), blast furnace enhancement (BOE), open hearth and electric arc furnace (EAF). Some of several SR processes developed according to the type of furnace involved are cited below.

- Basic oxygen furnace(BOF) : Corex, Finex, Hismelt, Dios, Combismelt, Coin
- Basic furnace hearth (BFH) : Tecnored, Kawasaki SR, Plasmasmelt
- Blast furnace enhancement (BFE) : Piragos, BSC Oxy-coal
- Open hearth (OH) : Ausmelt, Rosmelt
- Electric arc furnace (EAF) : Inred, Elred

2.9 Reduction kinetics

Basically reduction of iron ore to iron is a three-step conversion process. In carbothermic reduction, carbon and temperature plays the important role.

Reduction of Iron ore by Carbon and carbon monoxide follows below given reactions [5,24];

$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$

3Fe2O3 + C → 2 Fe3O4 + CO

Fe3O4 + 4C → 3 Fe + 4CO

Fe0 + C → Fe + CO

C + CO2 → 2CO

3Fe2O3 + CO → 2Fe3O4 + CO2

Fe3O4 + CO → 3FeO + CO2

FeO + CO → Fe + CO2

2.10 Plasma smelting and reduction

Past research shows smelting and reduction of different materials were fruitfully done by utilizing plasma technology. Some of those precious works that led to be an alternative solution for improved economy are mentioned below.

Carbothermic reduction and smelting of Ta_2O_5 with argon plasma-arc heating and hydrogen-argon plasma-arc melting was investigated [7]. Ductile Ta metal with greater purity level under different conditions was inspected.

Beach sand collected from east cost of India containing ilmenite was plasma smelted with petroleum coke as reductant [9]. TiO_2 containing slag and pig iron were obtained as final product. Effect of reductant percentage, input power and slag characteristics had been studied.

Carbothermic reduction and smelting of niobium pentoxide was done by using dc extended arc plasma reactor [10]. Final product obtained when examined found to be more than 97% Nb with

86% overall recovery. Nb along with carbon in the form of carbide was detected in characterization.

Plasma smelting of red mud a by-product of Bayer process was done to produce pig iron effectively [17]. Extended plasma arc reactor was used for the smelting operation. Study of different process parameters were observed and optimized.

Ilmenite was treated by thermal plasma with methane and ammonia as plasma forming gases [10]. High concentration of methane favoured in the formation of iron as well as titanium nitride and carbonitride.

Carbothermic reduction and smelting of silimenite was carried out in in transferred arc reactor with nitrogen as plasma gas [20]. Conversion of silimenite to Mullite, aluminium, silicon and silicon carbide was investigated.

Addition of zirconia in carbothermic reduction and smelting of iron ore fines by extended arc plasma was investigated [22]. Utilization of zirconia gave rise to nodularization of graphite in cast iron that possesses very good mechanical property.

Blue dust was smelted in extended arc plasma with coal and coke as reductants [23]. Magnesium was added in the melt stage. Purer pig iron having low content of sulphur and other tramp elements was obtained that can be comparable to SG iron.

Chapter 3

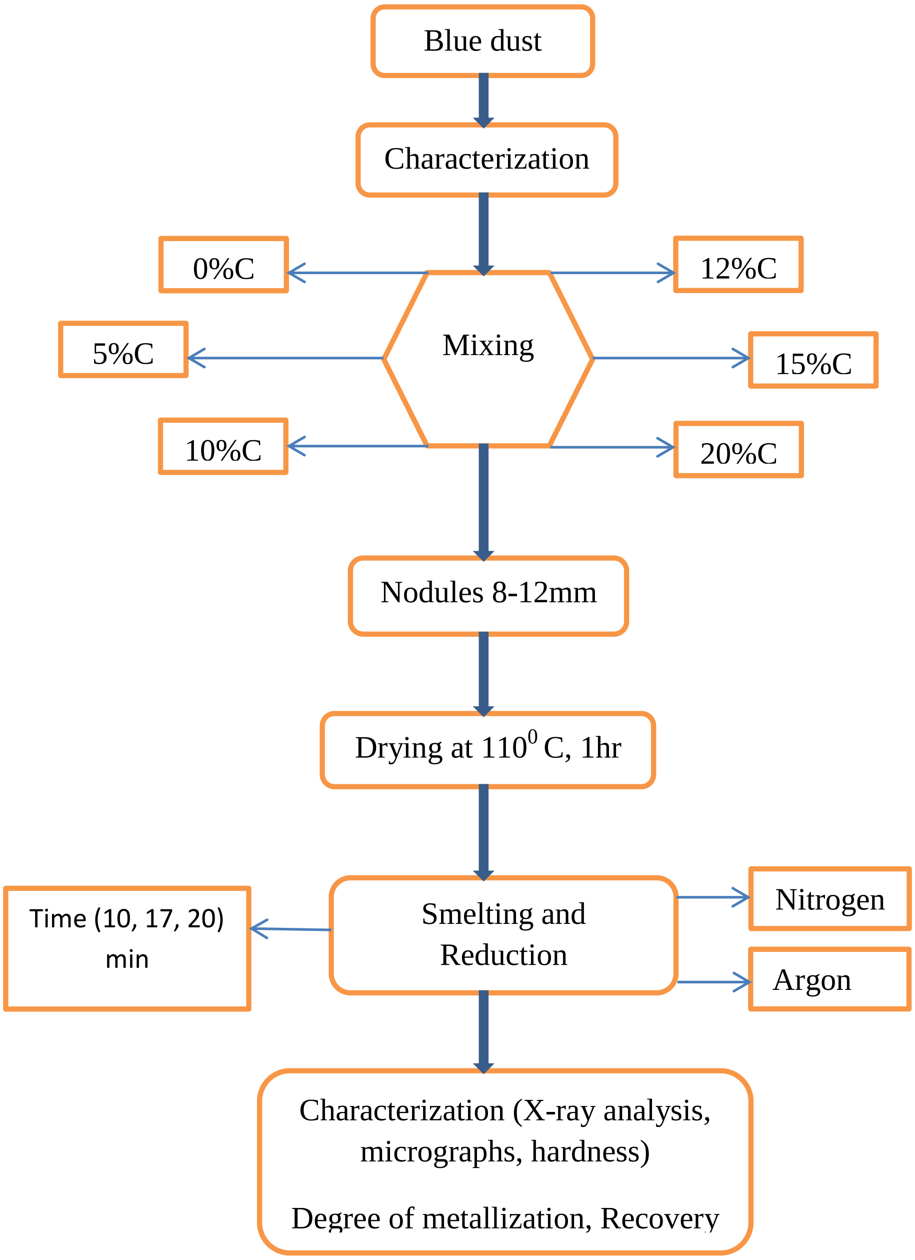
Experimental set up and Methodology

- Introduction
- Characterization of raw blue dust
- Preparation of feed material
- Smelting and reduction in DC arc plasma furnace
- Characterization of smelted and reduced product
- Degree of metallization

Chapter 3
Experimental set up and Methodology

3.1 INTRODUCTION

This chapter describes about procedure of experimental process adopted to reduce the blue dust with different composition and operating parameters into pig iron and to characterize each. Skeleton of experimental procedure is given below.



Before smelting and reduction, some basic process required for feed material i.e. compositional analysis, X-ray diffraction studies, preparation of nodules, drying. After plasma smelting, the final product have been subjected to a series of characterization test i.e. microstructural characterization of the surfaces, X-ray diffraction studies, degree of metallization studies, calculation of percentage of recovery, micro-hardness measurement. Each process is briefly described here.

3.2 Characterization of raw blue dust

3.2.1 Compositional analysis

The compositional analysis of raw blue dust powder was carried out in the export chemical unit of DISIR, Rajgangpur, India by preparing suitable stock solution and by following wet chemical analysis. For detection of weight fraction of presence of each element/oxide separate tests were followed. Loss on ignition percentage was determined by heating the raw blue dust at 1000^0 C for 1hour and calculating as following;

LOI in % = (Weight loss of material due to heating/Initial weight of material taken) × 100

3.2.2 X-ray diffraction studies

X-ray diffraction technique was used to detect the different phases presents in the raw sample collected from DISIR, Rajgangpur, India. XRD analysis was done by using X-Pert MPD system (PAN Analytical). Here Ni-filtered Cu-Kα radiation used in X-ray diffractometer. The d-spacing values obtained from XRD patterns were matched with the characteristic d-spacing of all possible values from JCPDS cards to obtain the various X-ray peaks.

3.3 Preparation of feed material

Six different weight percentages of blue dust and petroleum coke were taken separately and mixed properly. Nodules of size 8-12 mm were prepared by adding water to mixed compositions. All the prepared nodules were then dried at 110^0 C for removal of moisture and to strengthen the same in order to minimize loss during feeding.

3.4 Smelting in DC arc plasma furnace

3.4.1 DC arc plasma furnace

Smelting and reduction of different compositions were done in 35KW DC arc plasma furnace in plasma division of DISIR, Rajgangpur, India. The plasma furnace set up is shown below in Fig.

Fig 3.2 DC arc plasma setup

The equipment consists of the following units:

1. Power supply and control unit.
2. Gas supply and control unit.
3. Gas flow control unit.
4. Cathode-anode alignment unit.
5. Steel casting including heat insulating linings.
6. Cables and accessories.

On top of the reactor plasma torch is attached in the downward direction. The plasma torch contains a hollow cylindrical graphite crucible with 145mm outer diameter, wall thickness 15mm and 300mm high that serves as the anode. Hollow graphite rod of 400mm long and 5mm inner and 35mm outer diameter serves as the cathode. Graphite rod end is tapered to a conical shape for superior electron emission. Hollow structure of cathode has designed to have provisions for gas flow. The material to be processed was placed in the anode crucible bed and the arc was initiated by shorting the cathode and the crucible bottom wall (graphite plate). The arc length was increased by raising the cathode rod up suitably within the crucible to heat the charge placed in the crucible. Power supply unit and power control unit is designed to vary necessary voltage and current and easy control of this helps in smooth conducting experiments. Voltage and current can be altered over a range of 0-50V and 0-300A respectively. Gas supply unit comprises of types of plasma forming gases i.e. hydrogen, oxygen, argon and nitrogen. Besides these gases helium, neon, carbon monoxide, carbon dioxide and also mixture of above can be utilized as plasma forming gas. Gas flow control consisting of digital indicators helps in not only measuring gas flow rate but also governing suitable flow of gases as per experiment performed and stands as a key parameter. Gas flow rate can be varied from 0-2.5 LPM. Heat insulating materials are placed in between steel casting and reaction chamber.

3.4.2 Smelting and reduction operation

This is consisting of several prerequisite steps to be done before feeding samples into the reaction chamber. Initially crucible was cleaned in order to avoid any other material contained in crucible to be reacted with samples. Hollow tapered graphite rod was fitted in such a way that it points towards centre of reaction chamber. After checking no leakage in crucible it was placed the space provided in steel casting. Bubble alumina was poured in spacing between reaction chamber and reaction chamber that acts as insulating medium of heat. Power supply then provided and proper arcing between cathode and anode was tested. Gas supply is then connected to the cathode passage and plasma forming gas was purged into the reaction chamber for 1minute to displace atmospheric air. After that power supply and plasma forming gas supply both supplied simultaneously and required voltage and current maintained. Then sample feed were poured into the hot reaction chamber as per our requirement. Composition, type of plasma forming gases and operating parameters of each sample are cited below in table 3.

Sample no.	% C mixed with blue dust	Smelting duration (min)	Sample weight (gm.)
Plasma forming gas : Nitrogen Gas flow rate : 2.5 lpm Operating parameter : 50V, 300A			
1	0	17	300
2	5	17	295
3	10	17	301
4	12	10	302
5	15	17	295
6	20	17	273
Plasma forming gas : Argon Gas flow rate : 2.5 lpm Opearating parameter : 50V, 300A			
7	5	20	297
8	10	17	300
9	12	17	268
10	15	17	296
11	20	17	270

Table 3.1 Composition, plasma gas and operating parameters

3.5 Characterization of smelted product

After successful smelting of samples in the furnace, final product was cooled in the furnace itself. Then those bulk products were removed from crucible and appropriate samples were prepared for characterization.

3.5.1X-Ray Diffraction Studies

X-ray diffraction technique was used to identify the different phases presents in the smelted product. XRD analysis was done by using Philips X-Pert MPD system (PAN Analytical). Here Ni-filtered Cu-Kα (1.54) radiation used in X-ray diffractometer. D-spacing values obtained from XRD patterns were compared with the characteristic d-spacing of all possible values from JCPDS cards to obtain the various X-ray peaks.

3.5.2Optical microscopic studies

Since final product obtained was in irregular shape, crushing those into 5-10mm size and mounting in cold setting resin was essential before following polishing stages. After proper polishing micrographs were studied by using Zeusius light emission electron microscope under suitable magnification. Area fraction analysis was done for all samples by using Axio vision software of version 4.8.

3.6 Hardness

Vickers hardness was performed in a LECO micro hardness tester LM248AT by using suitable load.

3.7 Degree of metallization

By taking 1gm powdered sample of each, preparing proper stack solution and following wet chemical analysis percentage of metallic Fe and percentage of total Fe were obtained. Metallic Fe includes sum of metal and metal carbides whereas total Fe counts sum of metal, metal carbides and metal oxides. Degree of metallization calculated as following:

Degree of metallization = (Metallic Fe) / (Total Fe)

Chapter 4

Results and Discussion

- Introduction
- Characterization of raw blue dust
- Recovery
- Degree of metallization
- Characterization of final product
- Micro hardness
- Discussion

CHAPTER 4
RESULTS AND DISCUSSION

4.1 INTRODUCTION

Smelting and reduction of blue dust was carried out in 35 KW dc arc plasma reactor by using petroleum coke as reductant. By using argon and nitrogen as plasma forming gases with different composition were taken for this purpose. Characterization of raw blue dust as well as final product was done and smelting and reduction performances of different feeds are investigated in terms of degree of metallization and recovery. The results presented and discussed in this chapter.

4.2 Characterization of raw blue dust

4.2.1Chemical Composition Analysis

Blue dust is collected from DISIR, Rajagangpur. The chemical composition analysis of major constituents of blue dust done in export chemical laboratory, DISIR is given in Table 4.1.

OXIDES	IN %
Fe2O3	96.87
SiO2	0.45
Al2O3	0.21
TiO2	Trace
MgO	Trace
LOI	1.48

Table no. 4.1 chemical compositions of blue dust

4.2.2 X-ray diffraction studies

X-ray diffractogram are taken to detect the different phases presents in the raw blue dust to ascertain phases present using a Philips X-Ray Diffractometer with Cu-Kα radiation. Fig 4.1 presents XRD analysis of raw blue dust powder, where Fe_2O_3 was found to be as major phase. Since from chemical analysis it is seen other compounds are in trace amount, their existence is not detected in X-ray diffractogram.

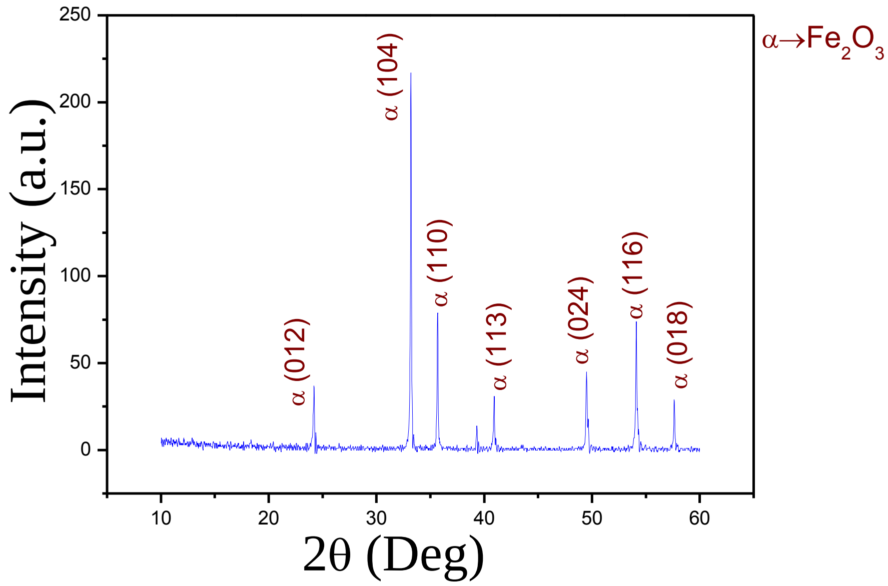


Figure 4.1 X-Ray diffractogram of blue dust raw powder.

4.3 Recovery

Percentage of recovery was calculated by taking ratio of weight of final product to weight of metal present in the composition before smelting and reduction. Fig 4.27 represents plot of variation of percentage of recovery w.r.t. %C in compositions. Curve representing samples smelted and reduced in nitrogen plasma lies above that of argon plasma. Comparatively higher percentage of recovery has been achieved by utilizing nitrogen as plasma gas.

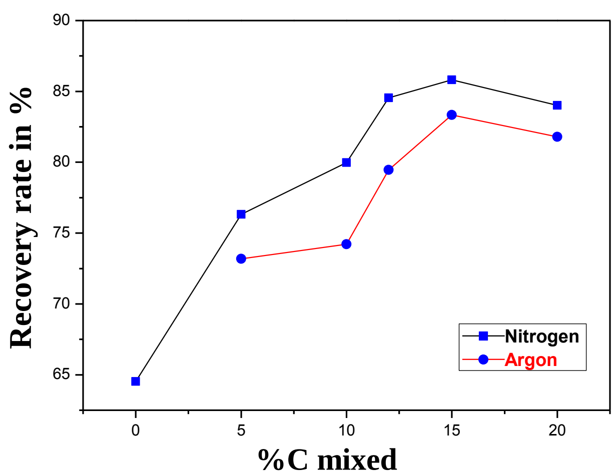


Figure 4.2 Percentage of recovery of samples smelted by argon and nitrogen plasma.

4.4 Degree of Metallization

Degree of metallization of all samples was calculated by following wet chemical analysis. Maximum degree of metallization i.e. about 98% was found in case of sample of blue dust mixed with 12% coke smelted by using nitrogen plasma. Degree of metallization of samples smelted by nitrogen plasma lies in the range of 88-98%. Meanwhile there is sharp fluctuation of degree of metallization curve observed in case of argon plasma. However, in both the cases, 12% C addition shows maximum degree of metallization

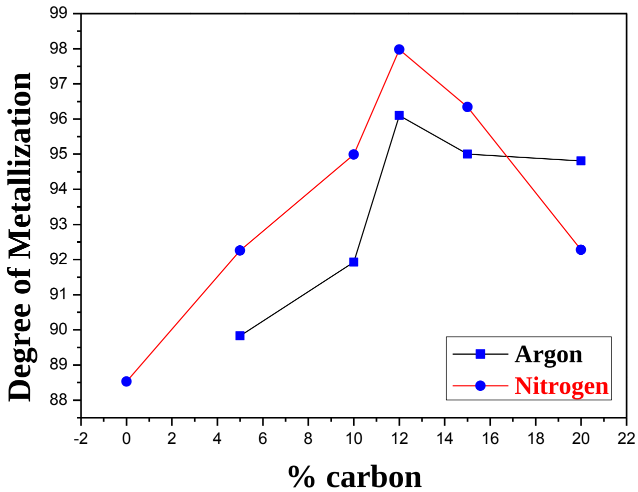


Figure 4.3 Degree of metallization of samples smelted by argon and nitrogen plasma.

4.5 Characterization of final product

4.5.1 Optical micrographic studies

Optical micrographs of all cold resin mounted polished samples were observed by using Zeusius light emission electron microscope under a constant magnification of 200X. Fig 4.13 to Fig 4.23 represents micrographs of all samples given below.

Fractured cementite phases are appeared to be elongated and randomly oriented in ferrite grains, Fig 4.4- 4.5- and Fig 4.11 . But, finer cementite phases are observed in case of Fig 4.8 and Fig 4.12; whereas in Fig 4.14 fine cementite with some pores is detected. In case of Fig 4.10, a porous mixture of ferrite and cementite is found. Fig 4.9 shows cementite-pearlite structure. Fig 4.7 coincides with ledeburite structure i.e. a mixture of cementite and pearlite. It may be due to rapid erosion of graphite from reaction chamber. In Fig 4.6 and Fig 4.13 needle like fractures along with fine cementite precipitates are revealed.

As in case of plasma smelting product is cooled from thousands of degree to room temperature, formation of cracks is seen in all smelted samples.

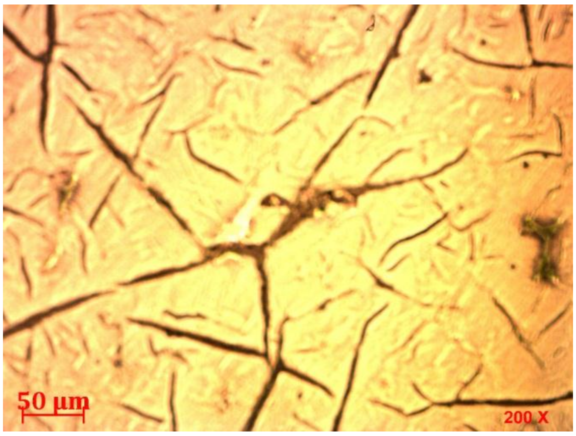


Figure 4.4 Optical micrograph of smelted blue dust + 0% coke by Nitrogen Plasma.

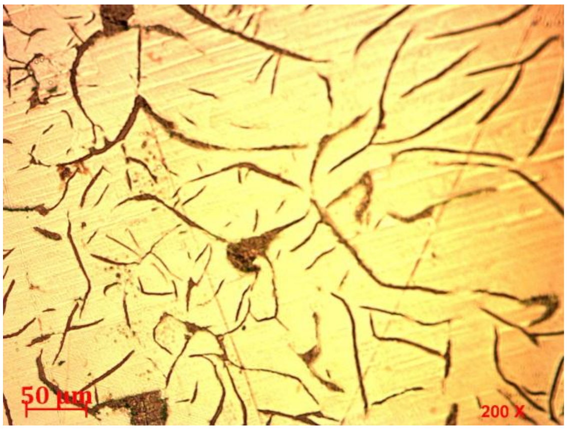


Figure 4.5 Optical micrograph of smelted blue dust + 5% coke by Nitrogen Plasma.

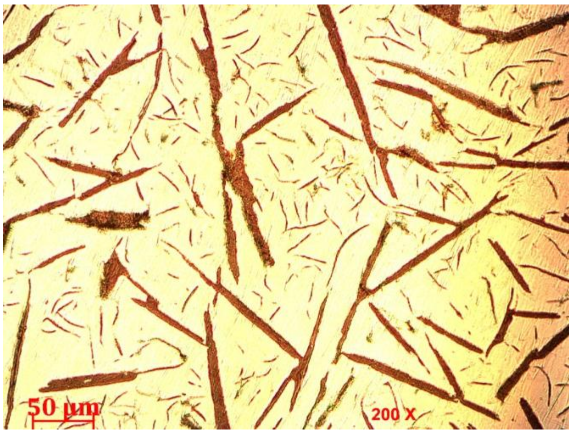


Figure 4.6 Optical micrograph of smelted blue dust + 10% coke by Nitrogen Plasma.

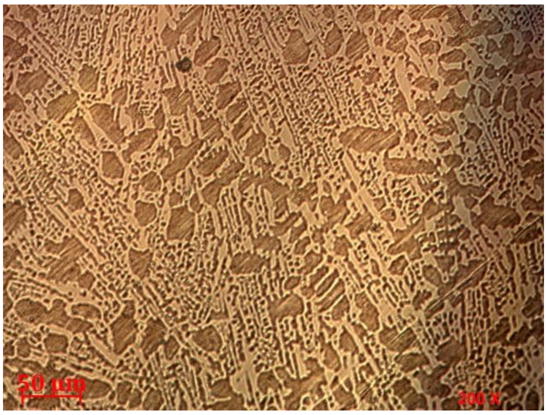


Figure 4.7 Optical micrograph of smelted blue dust + 12% coke by Nitrogen Plasma.

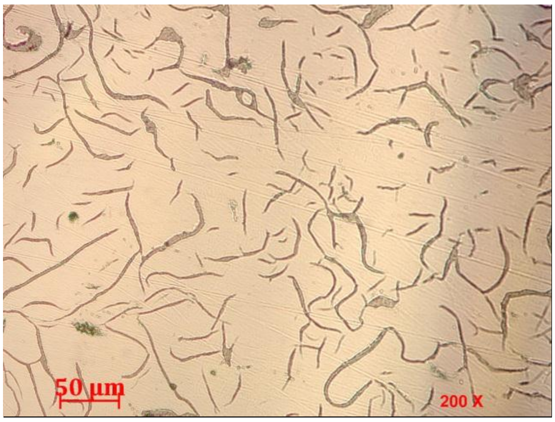


Figure 4.8 Optical micrograph of smelted blue dust + 15% coke by Nitrogen Plasma.

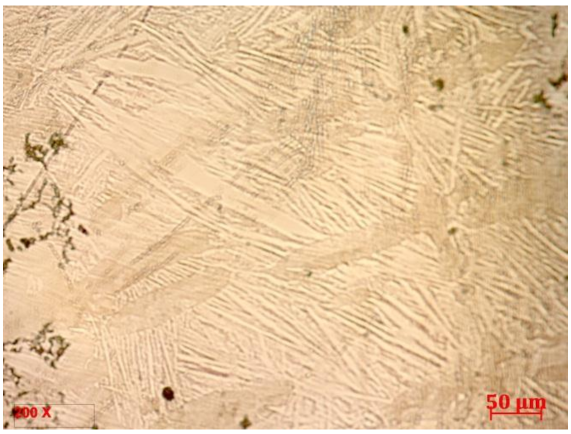


Figure 4.9 Optical micrograph of smelted blue dust + 20% coke by Nitrogen Plasma.

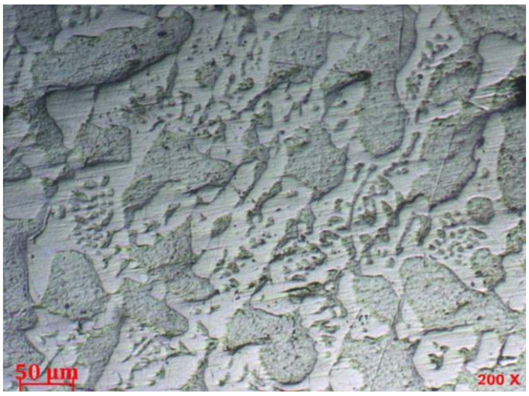


Figure 4.10 Optical micrograph of smelted blue dust + 5% coke by Argon Plasma.

Figure 4.11 Optical micrograph of smelted blue dust + 10% coke by Argon Plasma.

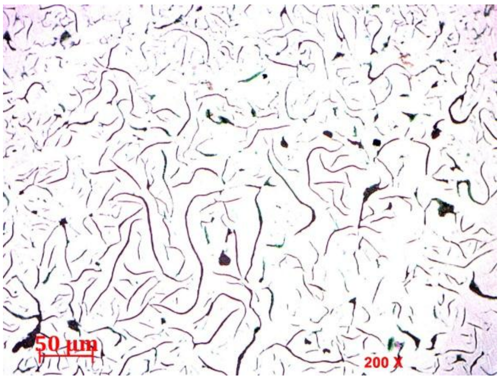


Figure 4.12 Optical micrograph of smelted blue dust + 12% coke by Argon Plasma.

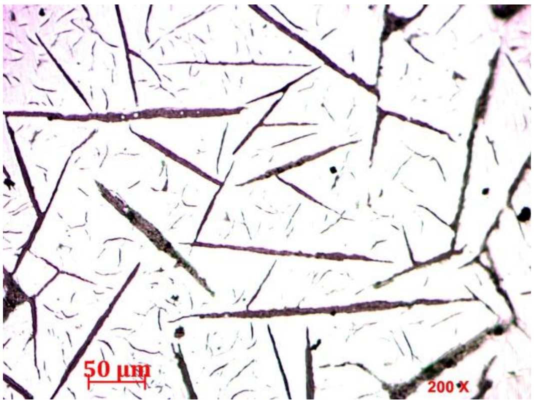


Figure 4.13 Optical micrograph of smelted blue dust + 15% coke by Argon Plasma.

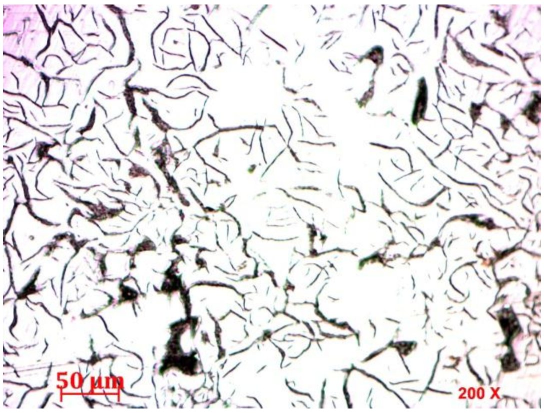


Figure 4.14 Optical micrograph of smelted blue dust + 20% coke by Argon Plasma

4.5.2 XRD analysis

XRD analysis of smelted and reduced compositions of blue dust and coke in plasma reactor by using argon and nitrogen as plasma gases are made to examine presences of phases in each. X-ray diffractogram of all samples are presented in Fig 4.2 to Fig 4.12. shown below and in all cases highest intensity peak shows presence of iron and other peaks shows presence of cohenite (cementite). Since graphite crucible was used as reaction chamber, decay of graphite bottom plate (more) and crucible walls (lesser) mainly occurs at high temperature and this extra carbon is dissolved into the molten feed and reduces iron oxide to iron which is confirmed from Fig 4.2. Besides iron another phase cementite is present in most cases. Formation of cementite is due to reaction of carbon with iron and wustite [25].

$$\mathbf{3Fe + C \rightarrow Fe_3C}$$

$$\mathbf{3FeO + 5CO\ (g) \rightarrow Fe_3C + 4CO_2\ (g)}$$

Again reaction of cementite with wustite can give rise to iron and carbon dioxide.

$$\mathbf{2FeO + Fe_3C \rightarrow 5Fe + CO}$$

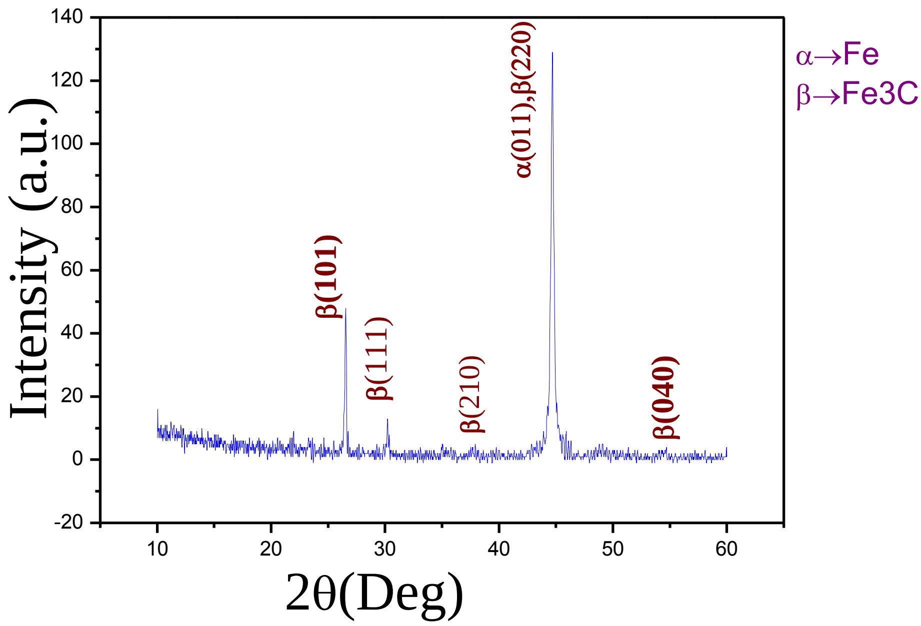


Figure 4.15 X-Ray diffractogram of smelted blue dust + 0% coke by Nitrogen plasma.

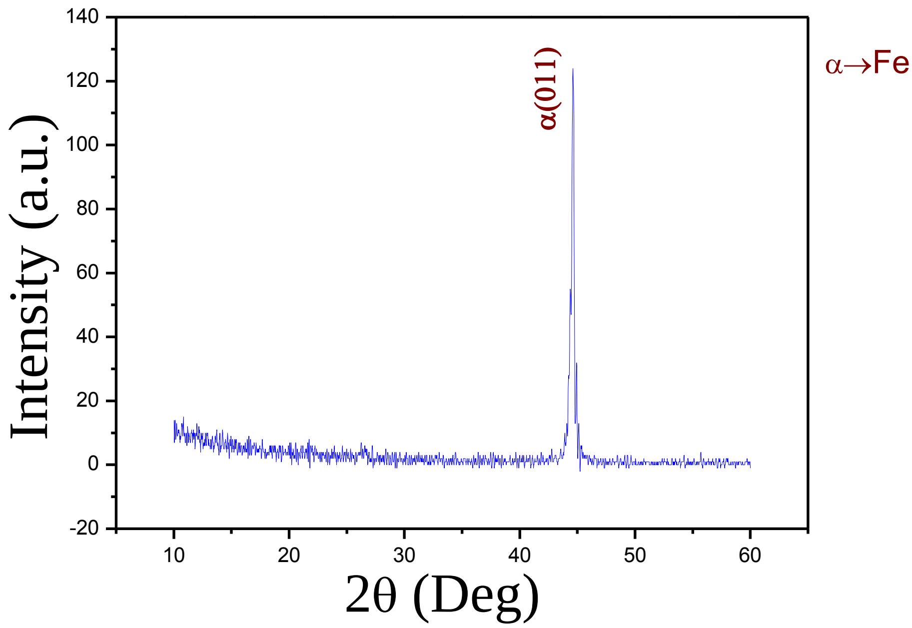


Figure 4.16 X-Ray diffractogram of smelted blue dust + 5% coke by Nitrogen plasma.

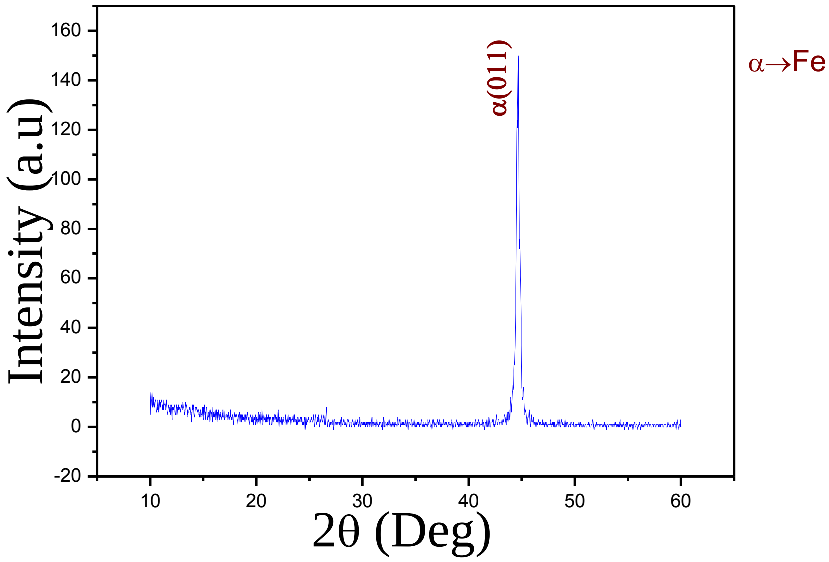


Figure 4.17 X-Ray diffractogram of smelted blue dust + 10% coke by Nitrogen plasma.

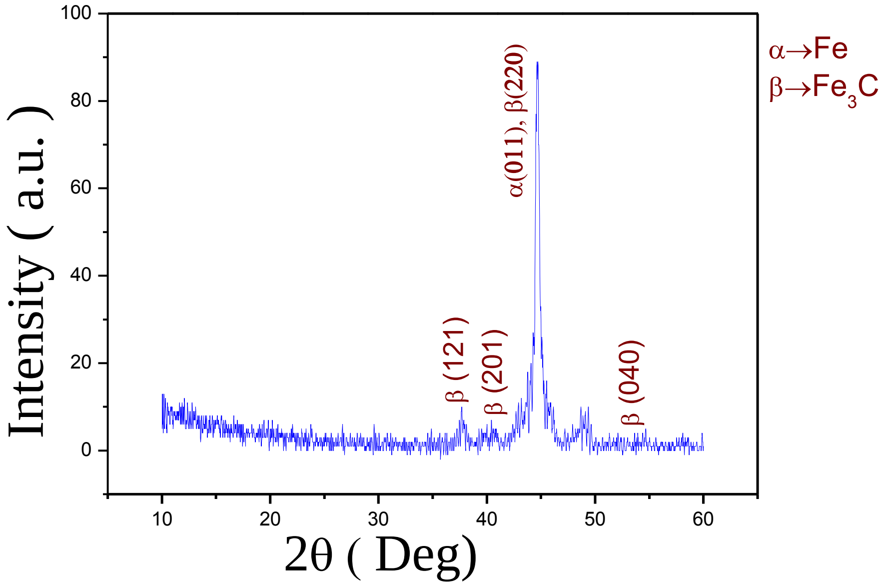


Figure 4.18 X-Ray diffractogram of smelted blue dust + 12% coke by Nitrogen plasma.

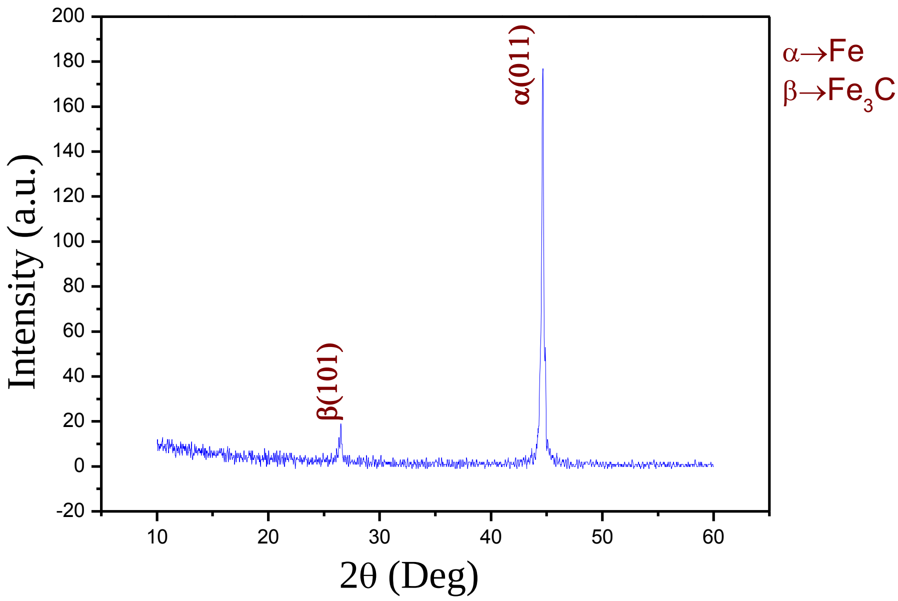


Figure 4.19 X-Ray diffractogram of smelted blue dust + 15% coke by Nitrogen plasma.

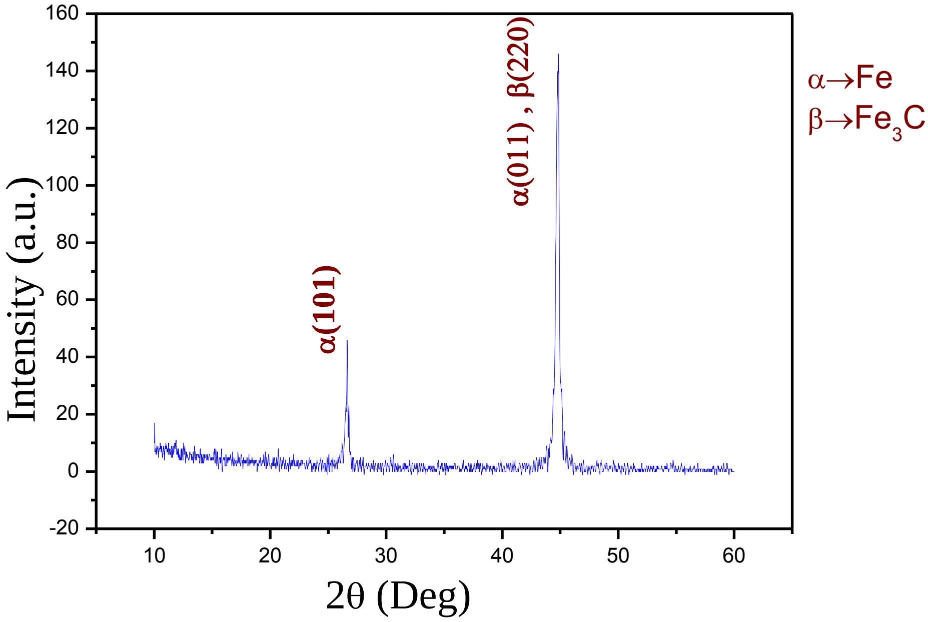


Figure 4.20 X-Ray diffractogram of smelted blue dust + 20% coke by Nitrogen plasma.

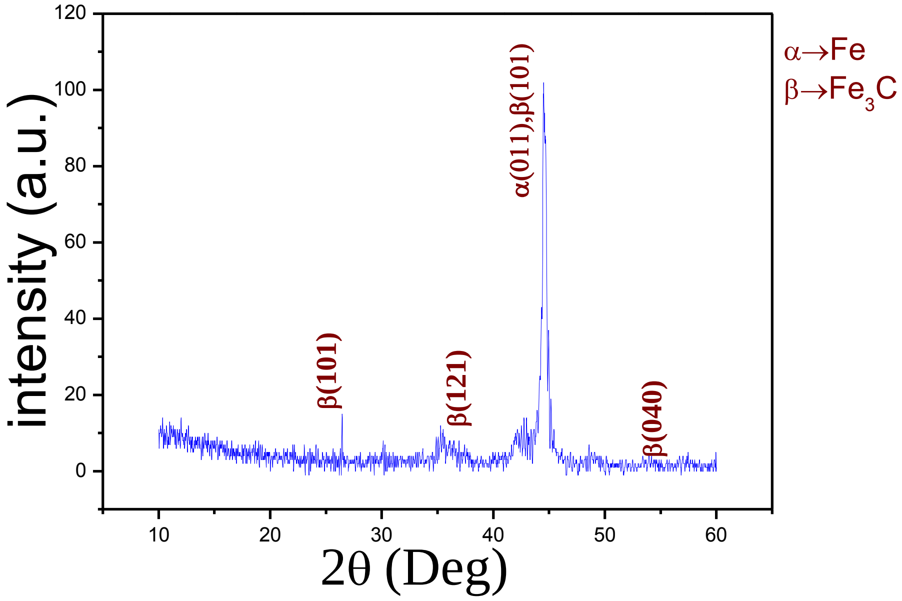


Figure 4.21 X-Ray diffractogram of smelted blue dust + 5% coke by Argon plasma.

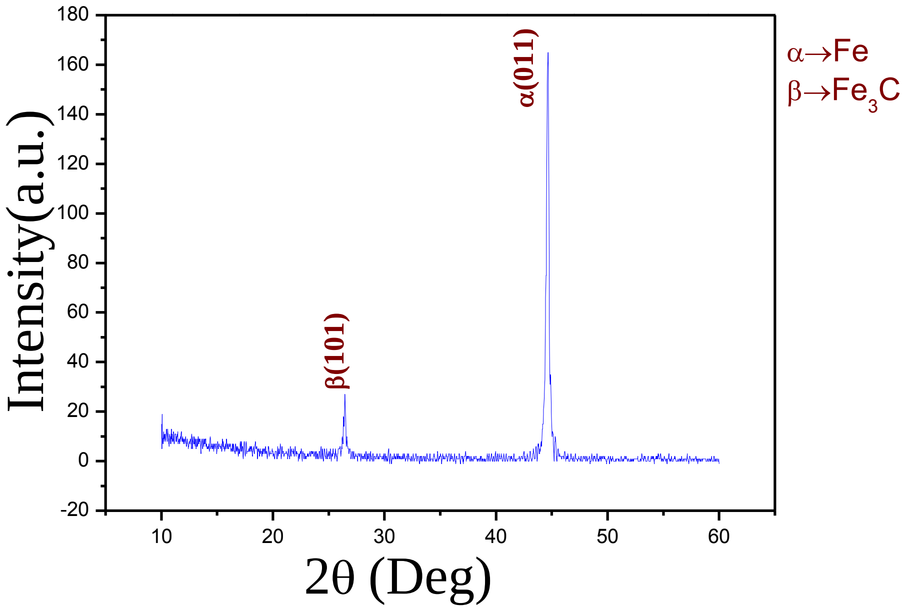


Figure 4.22 X-Ray diffractogram of smelted blue dust + 10% coke by Argon plasma.

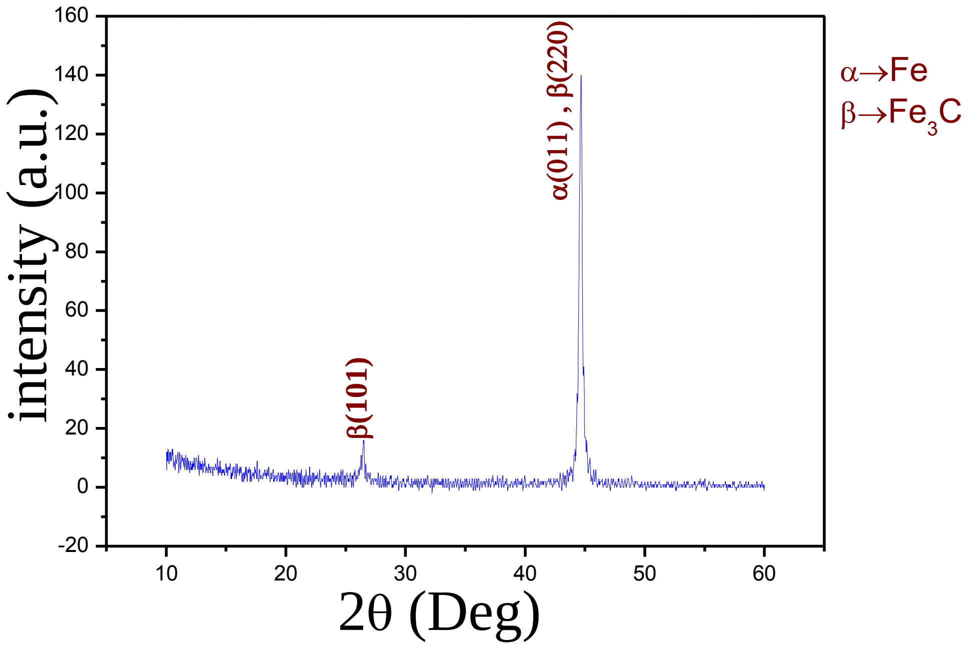


Figure 4.23 X-Ray diffractogram of smelted blue dust + 12% coke by Argon plasma.

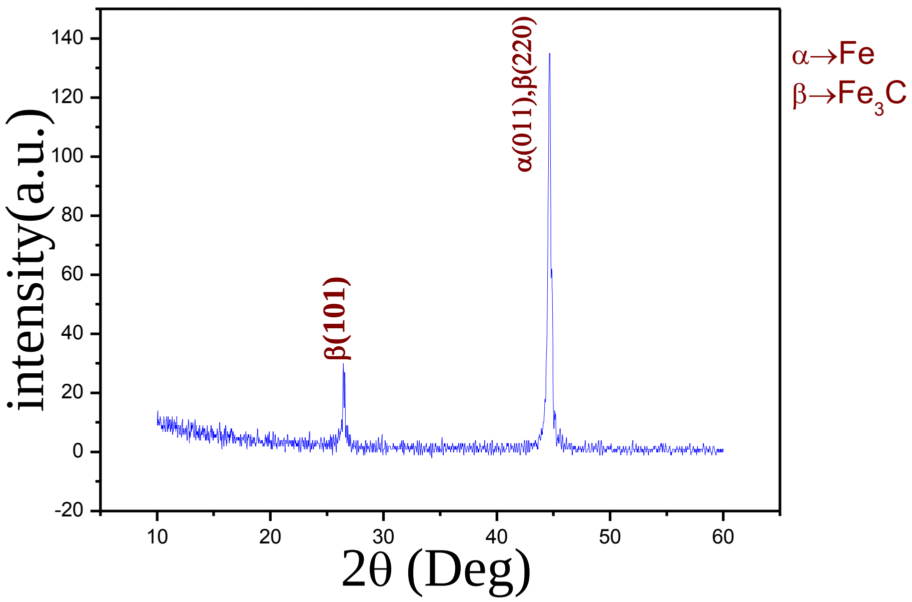


Figure 4.24 X-Ray diffractogram of smelted blue dust + 15% coke by Argon plasma.

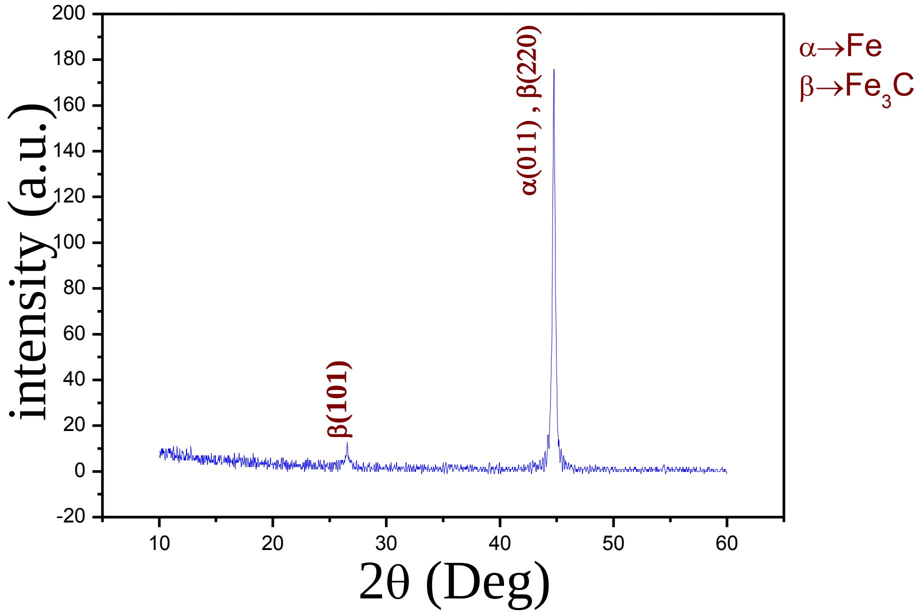


Figure 4.25 X-Ray diffractogram of smelted blue dust + 20% coke by Argon Plasma.

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4.4 Vickers hardness

Vickers hardness of smelted samples was performed by using a LECO micro hardness tester LM248AT taking 300gf load and dwell time of 10 second. Three different values of hardness are obtained i.e. 147, 208 and 312, is due to presence of ferrite, pearlite and cementite phases respectively depending on microstructure shown in micrographs. Meanwhile when hardness measured on needle like and elongated phases as seen in Fig, sample gets distorted and resulting hardness values varied from 50 to 80 HV.

4.7 Discussions

Recovery percentage is more in case of nitrogen plasma as compared to that of argon plasma. Nitrogen being diatomic gas and for which total heat of system (enthalpy) is affected i.e. increase to a greater extent is the key reason for higher rate of reduction and recovery. By adding 15% carbon to blue dust when smelted, gives rise to maximum recovery in both cases.
Maximum degree of metallization is achieved with 12% carbon (reductant) addition to blue dust.

From X-ray patterns and optical micrographs it is clear that, reduction of blue dust is enhanced by graphite erosion from the crucible and bottom plate. All samples smelted in argon plasma favours in cohenite formation, as cohenite is detected to be present in all cases.

In both cases percentage of cementite increases gradually and this increment is higher in case of nitrogen plasma smelted samples as compared to that of argon plasma. Fig 4.16 is the exception since erosion of crucible was more. When smelting duration is increased, formation of cementite is also increased.
Blue dust with different carbon percentage (i.e. 0, 5, 10, 12, 15 and 20) smelted by using nitrogen plasma shows the change of ferrite, ferrite-cementite to fully pearlite structure which can be attributed to Hull-Mehl model.
The variation in hardness of all smelted samples is due to presence of ferrite, pearlite, cementite and fractured cementite phases.

Chapter 5

Conclusions

Chapter 5
Conclusions

The conclusions drawn from the present investigation are as follows:

- Pig iron can be produced by plasma smelting of blue dust with coke as reductant.
- Recovery rate and degree of metallization is affected with carbon addition and type of plasma forming gas used, i.e. argon and/or nitrogen.
- Maximum recovery of 86% is obtained with the sample smelted in nitrogen plasma with addition of 15% carbon.
- Maximum degree of metallization of 98% is achieved for the sample smelted in nitrogen plasma with 12% carbon addition.
- X-ray diffractograms shows the presence of two different phases Fe and Fe_3C in case of all smelting experiments.
- Different type of microstructure is observed for samples depending on smelting parameters considered.
- Three different hardness values obtained is corroborated to the presence of ferrite, pearlite and cementite and fractured cementite phases as observed in microstructure.

SCOPE FOR FUTURE WORK:

The present piece of research work provides choice for future investigators to explore the possibility of utilization of plasma with increased output by altering more operating parameters that can produce value added products from wastes with economy.

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